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TRANSMITTAL OF PRIORITY DOCUMENT

Sir:

Enclosed is a copy of the certified priority document for the above-identified application. If there are any questions regarding this matter that need to be resolved, the Examiner is respectfully invited to contact the Applicants' attorney at the telephone number given below. Thank you for your time and attention to this matter.

Respectfully submitted,

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Bescheinigung | Certificate | Attestation

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The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

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For the President of the European Patent Office

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Page 2 de l'attestation

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Water-based catalyst inks and their use for manufacture of catalyst-coated substrates

The present invention relates to the field of electrochemical cells and fuel cells, more specifically to polymer-electrolyte-membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC). The invention describes novel water-based catalyst inks useful for manufacturing catalyst-coated substrates especially for membrane fuel cells.

Fuel cells convert a fuel and an oxidising agent into electricity, heat and water at two spatially separated electrodes. Hydrogen or a hydrogen-rich gas can be used as the fuel and oxygen or air as the oxidising agent. The energy conversion process in the fuel cell is distinguished by particularly high efficiency. For this reason, fuel cells are gaining increasing importance for mobile, stationary and portable applications.

The polymer electrolyte membrane fuel cell (PEMFC) and the direct methanol fuel cell (DMFC, a variation of the PEMFC, powered directly by methanol instead of hydrogen) are suitable for use as energy converting devices due to their compact design, their power density and high efficiency. The technology of fuel cells is broadly described in the literature, see for example K. Kordesch and G. Simader, "Fuel Cells and its Applications", VCH Verlag Chemie, Weinheim (Germany) 1996.

The basic element of a fuel cell is a so-called membrane-electrode-assembly (MEA). This comprises a membrane consisting of a proton-conducting polymer. This material will be referred to in the following also as ionomer. Both opposing faces of the electrolyte-membrane are in contact with catalyst layers which catalyze the electrochemical reactions. One of the catalyst layers forms the anode and the other forms the cathode of the membrane-electrode-assembly. At the anode hydrogen is oxidized and at the cathode oxygen reacts with the protons which have travelled through the ionomer membrane to yield water and electricity.

A catalyst-coated membrane (hereinafter abbreviated "CCM") comprises a polymer electrolyte membrane which is provided on both sides with a catalytically active layer. One of the layers takes the form of an anode for the oxidation of hydrogen and the second layer takes the form of a cathode for the reduction of oxygen. As the CCM consists of three layers (anode catalyst layer, ionomer membrane and cathode catalyst layer), it is often referred to as "three-layer MEA".

Gas diffusion layers (GDLs), sometimes referred to as gas diffusion substrates or backings, are placed onto the anode and cathode layers to bring the gaseous reaction media (hydrogen and air) to the catalytically active layers and, at the same time, to establish an electrical contact. GDLs usually consist of carbon-based substrates, such as carbon fibre paper or woven carbon fabric, which are highly porous and allow the reaction gases a good access to the catalyst layers. Furthermore, the gas diffusion layers must be able to supply humidifying water to the anode and remove reaction water from the cathode without their pores system being blocked by flooding with water. For avoiding flooding of the pores of the gas diffusion layers they are impregnated with hydrophobic polymers, e.g. with polytetrafluoroethylene (PTFE). GDLs can be tailored specifically into anode-type GDLs or cathode-type GDLs, depending on which side they are built into a MEA.

The carbon substrates from which the GDLs are manufactured exhibit a quite coarse surface. Therefore, in order to improve the contact of the GDLs to the catalyst layers of the fuel cell the GDLs can be coated with a so-called microlayer. The microlayer usually consists of a mixture of electrically conducting carbon black and a hydrophobic polymer, e.g. polytetrafluoroethylene (PTFE) and smoothes the coarse surface structure of the carbon substrates.

According to the above description of a membrane-electrode-assembly it comprises five layers: a central polymer electrolyte membrane, two catalyst layers and two gas diffusion layers.

The polymer electrolyte membrane comprises proton-conducting polymer materials. These materials are also referred to below as ionomers. Tetrafluoroethylene-fluorovinyl-ether copolymer with sulfonic acid groups is preferably used. This material is marketed for example by E.I. DuPont under the trade name Nafion®. However, other, especially fluorine-free, ionomer materials such as sulfonated polyether ketones or aryl ketones or polybenzimidazoles may also be used. Suitable ionomer materials are described by O. Savadogo in "Journal of New Materials for Electrochemical Systems" I, 47-66 (1998). For use in fuel cells, these membranes generally have a thickness of from 10 to 200 μm. Generally, the surface of the polymer electrolyte membranes is hydrophilic, however, advanced materials with hydrophobic surfaces are also known.

The anode and cathode catalyst layers contain electrocatalysts, which catalyse the respective reaction (oxidation of hydrogen at the anode and reduction of oxygen at the cathode). The metals of the platinum group of the periodic table are preferably used as

the catalytically active components. For the most part, supported catalysts are used, in which the catalytically active platinum group metals have been fixed in nano-sized particle form to the surface of a conductive support material. The average particle size of the platinum group metal is between about 1 and 10 nm. Carbon blacks with particle sizes of 10 to 100 nm and high electrical conductivity have proven to be suitable as support materials.

There have been disclosed various ways of manufacturing a complete membrane-electrode-assembly (MEA) consisting of five layers: The anode GDL, the anode catalyst layer, the ionomer membrane, the cathode catalyst layer and the cathode GDL. For example, the electrolyte membrane can first be coated on both sides with the requisite catalyst layers yielding a so-called catalyst-coated membrane (CCM). To produce a membrane electrode assembly therefrom, GDLs have to be placed on top of the catalyst layers and laminated thereto. Alternatively, the catalyst layers can be coated first onto the gas diffusion layers to yield so-called catalyst coated backings (CCBs). An electrolyte membrane is then placed between two catalyst coated backings and a firm contact between all three components is established by applying heat and pressure.

Thus, a MEA can be manufactured by combining a CCM (catalyst-coated membrane) with two GDLs (on the anode and the cathode side), or alternatively, by combining an ionomer membrane with two catalyst-coated backings (CCBs) at the anode and the cathode side. In both cases, a five-layer MEA product is obtained. These two manufacturing schemes may be combined, if suitable.

The present invention deals with water-based catalyst inks and their use for production of catalyst-coated substrates (such as CCBs, CCMs and the like). For producing a CCB, a catalyst ink is prepared which is a pasty substance comprising the electrocatalyst, an ionomer, solvents and optionally other ingredients, e.g. hydrophobic polymer binder, pore-forming agents etc. This ink is then applied using a suitable technique to the surface of the gas diffusion layer and cured by heating. The thus prepared catalyst-coated backings (CCBs) can be combined with an ionomer membrane to form a membrane- electrode-assembly.

The solvents used for preparing the ink usually comprise water and organic solvents. Depending on the content of water one can distinguish water-based inks, wherein water forms the major part of the solvents used, and inks wherein organic solvents form the major part.

US 5,869,416 discloses catalyst inks which are based predominantly on organic solvents such as propylene carbonate, ethylene carbamate and the like. However, water-based inks are mostly preferred because they are not subject to stringent occupational safety and health standards.

In US 4,229,490, a method for catalyst application to an electrode substrate is proposed, using a catalyst ink which contains Pt black, graphite, PTFE, water and Triton-X as a surfactant. Due to the high boiling point and low vapour pressure of the Triton-X, separate washing and rinsing steps had to be employed in order to remove the surfactant after printing and drying.

US 5,211,984 describes catalyst layers prepared using polyvinyl alcohol (PVA). The surfactant nature of the PVA provides for adaequate dispersion among the supported catalyst particles in an aqueous solution and the molecular structure acts to bind the carbon particles and Nafion agglomerates so that strong films are obtained with low weight fractions of PVA. PVA is a polymer material, which must be decomposed by heat or washed by water to remove it from the catalyst layer.

US 6,127,059 describes the use of Triton X-100 surfactant for preparing an ink comprising carbon black and polytetrafluoroethylene (PTFE). This ink is used to coat a carbon cloth substrate. Thereafter the cloth is dried and heated for 30 minutes at 370 °C to melt the PTFE and, at the same time, decompose and remove the surfactant.

EP 0 731 520 A1 describes a catalyst ink comprising an electrocatalyst, ionomer and water as a solvent. This ink comprises apart from the ionomer no further organic components. DE 100 37 074 A1 discloses a catalyst ink comprising an electrocatalyst, an ionomer, water and an organic solvent wherein the organic solvent is at least one compound from linear di-alcohols with a flashpoint above 100 °C which are present in the ink in an amount ranging from 1 to 50 wt.-% relative to the weight of water.

When trying to coat hydrophobic substrates, such as backings or polymer films, with hydrophilic water-based inks, a severe wetting problem arises especially when the coating has to be applied in a large format. The printed ink tends to accumulate and form islands so that several consecutive coating passes are necessary to achieve a uniform coating. This is very time-consuming and costly.

Based on the foregoing, there is a need in the art for coating hydrophobic backings and other substrates with water-based inks without the wetting problems just described. Therefore it is an object of the present invention to provide a process for manufacturing

catalyst-coated substrates with a water-based catalyst ink without the necessity of employing several coating passes for overcoming the repellency property of the hydrophobic surface of the substrate. A further object of the present invention is to provide a suitable catalyst ink for this process.

For a better understanding of the present invention together with other and further advantages and embodiments, reference is made to the following description taken in conjunction with the examples, the scope of which is set forth in the appended claims.

The present water-based catalyst inks include a surfactant. The present inventors have found that highly volatile surfactants having a vapour pressure at ambient temperature (approx. 20 - 25 °C) of from 1 to 600 Pa are suitable for this purpose. The use of such a surfactant allows the application of the water-based ink to the hydrophobic surface of a substrate. The required coating deposit ("lay-down") can be achieved in a single coating pass and the resulting catalyst layer exhibits no reduction in performance due to residual surfactant in the layer. At the drying temperatures used during the coating process the surfactant evaporates from the ink without any residue in the catalyst layer.

Figure 1 shows the U/I performance curves (cell voltage vs. current density) for an MEA manufactured using the catalyst ink according to the invention (example 1) compared to an MEA made using a conventional catalyst ink (comparative example).

The present invention describes new water-based inks containing a special type of surfactant. This surfactant improves the wetting characteristics of the ink, particularly to hydrophobic substrate materials, such as, e.g., polymer films, advanced ionomer membrane materials or PTFE-impregnated backings. The relatively high vapour pressure facilitates the removal of the surfactant during the drying stage e.g. at temperatures from 50 to 150 °C. As a consequence, less surfactant remains in the printed electrode layers; this in turn leads to an improvement in electrical performance of the MEAs manufactured with these inks. In contrast thereto, a surfactant with a low vapour pressure (i.e. below 1 Pa), for example, octyl-phenoxy-polyethoxylates such as Triton X-100, manufactured by Rohm & Haas Co., remains in the printed electrode after the drying process and deactivates the catalyst layer.

Suitable surfactants for use in the present invention are those having a vapour pressure in the range of 1 to 600 Pa, preferably in the range of 100 to 500 Pa and most preferably of 200 to 400 Pa at ambient temperature (approx. 20-25 °C). Examples for suitable classes of surfactants are non-ionic, anionic or cationic surfactants, such as fluorinated

wetting agents (Fluorad™ types, manufactured by 3M Co.), tetramethyl-decyn-diol-based wetting agents (Surfynol™ types, manufactured by Air Products and Chemicals Inc.), soy-lecithin-based wetting agents or phospho-amino-lipoides and the like. The vapor pressure of the materials can be determined by standard techniques. Lists of such data are also available e.g. in "CRC Handbook of Chemistry and Physics", CRC Press LLC, Boca Raton (USA).

The catalyst ink comprises electrocatalyst, ionomer and water as a main solvent in addition to the surfactant. The amount of surfactant is usually in the range of 0.1 to 20 wt.-% based on the total composition of the catalyst ink. In addition, the water-based ink may contain organic solvent, additives, defoamers, pore-forming agents, preservatives, and the like. Mixtures of the listed ingredients as well as mixtures of various surfactants may also be used.

Suitable electrocatalysts are e.g. carbon black supported precious metal-based catalysts such as Pt/C or PtRu/C. However precious metal powders and precious metal blacks as well as inorganic oxides containing precious or non-precious metals can be used.

The water-based catalyst ink contains 5 to 75 wt.-% of electrocatalyst, 10 to 75 wt.-% of ionomer solution (water-based or organic solvent-based), 10 to 75 wt.-% of (e.g. deionized) water, 0 to 50 wt.-% of organic solvent and 0.1 to 20 wt.-% of surfactant with a vapour pressure of 1 to 600 Pa. Suitable organic solvents are glycols (e.g. ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, butanediol and mixtures thereof), alcohols (e.g. C_{1-4} alcohols and mixtures thereof), esters (e.g. esters of a C_{1-4} alcohol with a C_{1-4} carboxylic acid and mixtures thereof), aromatic solvents (e.g. benzene or toluene) and aprotic polar solvents (e.g. N-methylpyrrolidone, ethylene carbonate, propylene carbonate, DMSO) and the like. Preferably glycols are employed.

The ionomer solutions are commercially available and typically comprise an ionomer in water or an organic solvent. Generally they contain 5 to 20 wt.-% ionomer. Depending on the type of electrocatalyst the weight ratio of ionomer to electrocatalyst is usually from 1:1 to 1:15, preferably from 1:1 to 1:10 and more preferably 1:2 to 1:6. The ionomer solution is diluted with water and optionally additional organic solvent to ensure that the resultant ink can be processed.

The process according to the invention for manufacturing a catalyst-coated substrate comprises the following steps:

a) providing a substrate with a hydrophobic surface (GDL, ionomer membrane etc.);

b) providing the above defined water-based catalyst ink; and
c) coating the hydrophobic surface of the substrate with said ink and drying the resulting catalyst-coated substrate.

The substrate is preferably selected from the group consisting of a polymer film, an ionomer membrane, a carbon fiber, a carbon cloth, a carbon felt or a paper-type material. The substrate can be present as an individual sheet or in continuous roll form.

Having now generally described the invention, the same may be more readily understood through reference to the following examples, which are provided by way of illustration and are not intended to limit the present invention.

EXAMPLES

Example

For manufacturing a membrane-electrode-assembly (MEA) according to the proposed process, water-based catalyst inks were prepared using Surfynol® from Air Products and Chemicals Co. as a surfactant. Surfynol® 420 has a vapor pressure at ambient temperature (22 °C) of approximately 270 Pa. As a source for the ionomer in the catalyst ink, a Nafion® solution in water was used. The ionomer was employed in its acidic form. The following inks were prepared for the cathode and anode:

Catalyst ink for the cathode:

13.0 g	Electrocatalyst Elyst A 40 (40 % Pt/C, OMG AG, Hanau)
50.0 g	Nafion® solution (11.4 wt.-% in water)
35.0 g	water (deionized)
2.0 g	Surfynol®420
100.0 g	

Catalyst ink for the anode:

14.0 g	PtRu-Electrocatalyst (40 % PtRu/C, OMG AG, Hanau)
48.0 g	Nafion® solution (11.4 wt.-% in water)
36.0 g	water (deionized)
2.0 g	Surfynol® 420
100.0 g	

The catalyst ink for the cathode was prepared by thoroughly mixing the catalyst with the Nafion® solution, water and surfactant by means of a high speed stirring device. This ink was coated onto a hydrophobic carbon fibre paper (HE-paper from SGL-Carbon) by screen printing in only one pass and dried in two steps: at 75° C for 3 minutes and at 95° C for 1 minute. The whole surface of the gas diffusion layer was evenly coated with the catalyst layer. The resulting cathode gas diffusion electrode (GDE) had a precious metal loading of 0.4 mg Pt/cm^2. In the same manner, the anode gas diffusion electrode was manufactured using the catalyst ink for the anode. The anode GDE had a precious metal loading of 0.3 mg Pt/cm^2 and 0.15 Ru/cm^2. As with the cathode GDE, only one coating pass was necessary to achieve an even coating over the whole surface of the carbon fibre substrate without island formation.

The thus produced cathode and anode GDEs were used to build an MEA (membrane electrode assembly). For that purpose an uncoated ionomer membrane (Nafion® 112; DuPont; thickness of membrane 50 μm) was placed between the anode and cathode GDEs. This assembly was then laminated under a pressure of 20 bar for the duration of 1 minute at a temperature of 150 °C.

Comparative example

For comparison, the catalyst inks were prepared in the same way as described in the example. Instead of Surfynol®, Triton X-100, which is widely used in the fuel cell industry, was used as a surfactant. This surfactant has a vapour pressure of less than 1 Pa at ambient temperature (22 °C). Thus, this surfactant is much less volatile than Surfynol®. With the two water-based catalyst inks a membrane-electrode-assembly was prepared in the same way as described in the preceding example.

Electrochemical tests

The membrane-electrode-assemblies from the example and the comparison example were inserted into a PEMFC single test cell with an active area of 50 cm^2 and their

electrochemical performances were measured using reformate as fuel gas for the anode and air for the oxidant at the cathode. The anode gas mixture contained 45 vol.-% H_2, 31 vol.-% N_2, 21 vol.-% CO_2 and 50 vol.-ppm CO with an additional air bleed of 3 vol.-%. The cathode of the test cell was supplied with air. The cell temperature was adjusted to 70 °C. Humidification of the anode was done at 80 °C and cathode humidification at 55 °C. The operating gas pressure was set to 1 bar (absolute). The stoichiometry of the reactants were adjusted to 1.1 for the anode gas and 2.0 for the cathode gas.

The measured cell voltages for selected current densities are listed in Table 1 and shown in figure 1. These results clearly demonstrate that the MEA manufactured using the catalyst ink according to the invention has a considerably improved electrochemical performance across the full current density range.

The surfactants Surfynol® 420 and Triton X-100 have different vapor pressures at ambient temperature. The vapor pressure of Surfynol® is significantly higher than that of Triton X-100. Therefore Surfynol® evaporates easily from the catalyst ink at the drying conditions applied. The remaining catalyst layer is substantially free of surfactant and consequently has a very good electrochemical performance. In contrast, Triton X-100 evaporates only slowly from the catalyst ink so that the dried catalyst layer still contains considerable amounts of the surfactant which is assumed to partially block the active sites of the electrocatalyst and thus leads to a poorer performance.

Table 1 Measured cell voltages (mV) for selected current densities of the membrane electrode assemblies from the example and from the comparison example

Current density [mA/cm^2]	100	500	900
Example [mV]	791	658	484
Comparison example [mV]	784	627	381

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Claims

1. A water-based catalyst ink comprising:
   5 to 75 wt.-% electrocatalyst;
   10 to 75 wt.-% of ionomer solution;
   10 to 75 wt.-% of water;
   0 to 50 wt.-% of organic solvent;
   and 0.1 to 20 wt.-% of surfactant with a vapour pressure at ambient temperature in the range of 1 to 600 Pascal (Pa).

2. The water-based ink according to claim 1, wherein the vapour pressure of the surfactant at ambient temperature is in the range of 100 to 500 Pa.

3. The water-based catalyst ink according to claim 2, wherein the surfactant is selected from the group consisting of fluorinated wetting agents, tetramethyl-decyn-diol-based wetting agents, soy-lecithin-based wetting agents or phospho-amino-lipoides or mixtures thereof.

4. The water-based ink according to claim 3, wherein the concentration of the surfactant is in the range of 0.1 to 10 wt.-% relative to the total weight of the catalyst ink.

5. A process for manufacturing a catalyst-coated substrate which comprises a hydrophobic surface and deposited thereon a catalyst layer, said process comprising the steps of:
   a) providing a substrate with a hydrophobic surface;
   b) providing a catalyst ink as defined in any one of claims 1 to 4; and
   c) coating the hydrophobic surface of the substrate with said ink and drying the resultant catalyst-coated substrate.

6. A process for manufacturing a gas diffusion electrode which comprises a hydrophobic gas diffusion layer and deposited thereon a catalyst layer, said process comprising the steps of:
   a) providing a hydrophobic gas diffusion layer;
   b) providing a catalyst ink as defined in any one of claims 1 to 4; and
   c) coating the gas diffusion layer with said ink and drying the resultant gas diffusion electrode.

7. The process according to claim 6, wherein prior to applying the catalyst layer, the hydrophobic gas diffusion layer is first coated with a microlayer and then dried and calcined.

8. The process according to any one of claims 5 to 7, wherein the surfactant of the water-based catalyst ink is removed at a drying temperature in the range of 50 to 150 °C.

9. The process according to claim 7, wherein the calcining is conducted at a temperature in the range of 200 to 400°C.

10. Use of the catalyst-coated substrates manufactured according to claim 5 for the production of a membrane-electrode-assembly for a fuel cell.

11. Use of the gas diffusion layer manufactured according to any one of claims 6 to 7 for the production of a membrane-electrode-assembly for a fuel cell.

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Abstract

The present invention relates to water-based catalyst inks and their use for manufacture of catalyst-coated substrates. The catalyst layer is applied to the hydrophobic surface of a substrate by using a water-based catalyst ink comprising an electrocatalyst, an ionomer and water. The catalyst ink further comprises a highly volatile surfactant having a vapour pressure at ambient temperature in the range of 1 to 600 Pa. The use of this surfactant allows applying the water-based ink to the hydrophobic surface of a variety of substrates, such as gas diffusion layers, advanced ionomer membranes or polymer substrates. The required coating deposit can be applied in only one coating pass and the resulting catalyst layer exhibits improved performance due to the absence of residual surfactant in the catalyst layer.

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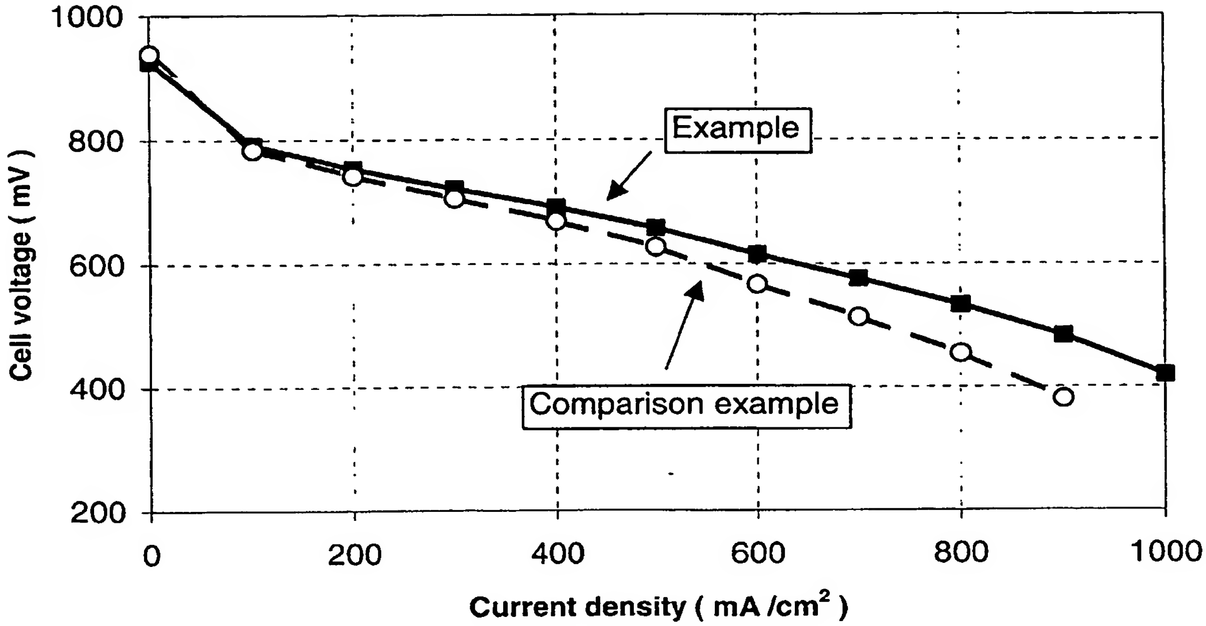

Figure 1